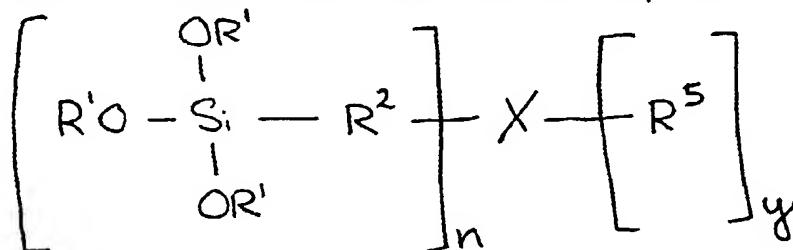


8/8/03

What we claim is:

1. A method of treating a metal substrate, comprising:
  - (a) providing a metal substrate; and
  - (b) applying a coating of a silane composition onto the metal substrate, said silane composition comprising at least one substantially unhydrolyzed aminosilane which has one or more secondary or tertiary amino groups.

2. The method of claim 1, wherein said aminosilane comprises:



wherein:

-n is either 1 or 2;

-y = (2-n);

-each R<sup>1</sup> is individually chosen from the group consisting of: C<sub>1</sub> - C<sub>24</sub> alkyl and C<sub>2</sub> - C<sub>24</sub> acyl;

-each R<sup>2</sup> is individually chosen from the group consisting of: substituted aliphatic groups, unsubstituted aliphatic groups, substituted aromatic groups, and unsubstituted aromatic groups;

-R<sup>5</sup> is chosen from the group consisting of: hydrogen, C<sub>1</sub> - C<sub>10</sub> alkylene, C<sub>1</sub> - C<sub>10</sub> alkylene substituted with one or more amino groups, C<sub>1</sub> - C<sub>10</sub> alkenylene, C<sub>1</sub> - C<sub>10</sub> alkenylene substituted with one or more amino groups, arylene, and alkylarylene;

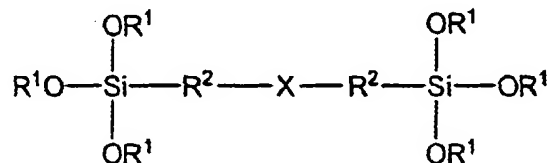
-X is either:



-wherein each  $R^3$  is individually chosen from the group consisting of:  
hydrogen, substituted and unsubstituted aliphatic groups, and substituted  
and unsubstituted aromatic groups; and  
- $R^4$  is chosen from the group consisting of: substituted and unsubstituted  
aliphatic groups, and substituted and unsubstituted aromatic groups; and  
5 wherein, when  $n=1$ , at least one of said  $R^3$  and said  $R^5$  is not hydrogen.

3. The method of claim 1, wherein said aminosilane comprises a bis-silyl  
aminosilane having two trisubstituted silyl groups, wherein the substituents are  
individually chosen from the group consisting of alkoxy, aryloxy and acyloxy.

10 4. The method of claim 3, wherein said bis-silyl aminosilane comprises:

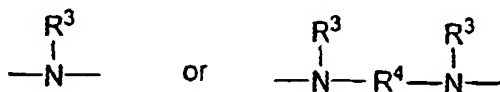


wherein:

-each  $R^1$  is individually chosen from the group consisting of:  $C_1 - C_{24}$  alkyl and  
 $C_2 - C_{24}$  acyl;

15 -each  $R^2$  is individually chosen from the group consisting of: substituted aliphatic  
groups, unsubstituted aliphatic groups, substituted aromatic groups, and  
unsubstituted aromatic groups; and

-X is either:



-wherein each  $R^3$  is individually chosen from the group consisting of: hydrogen, substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and

- $R^4$  is chosen from the group consisting of: substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups.

5        5.     The method of claim 4, wherein each  $R^1$  is individually chosen from the group consisting of: ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.

10       6.     The method of claim 4, wherein X is chosen from the group consisting of: a C-Si bond,  $C_1 - C_6$  alkylene,  $C_1 - C_6$  alkenylene,  $C_1 - C_6$  alkylene substituted with at least one amino group,  $C_1 - C_6$  alkenylene substituted with at least one amino group, arylene, and alkylarylene.

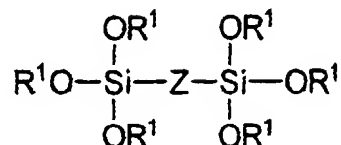
15       7.     The method of claim 4, wherein each  $R^2$  is individually chosen from the group consisting of: hydrogen, ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.

20       8.     The method of claim 1, wherein said aminosilane is chosen from the group consisting of: *bis*-(trimethoxysilylpropyl)amine, *bis*-(triethoxysilylpropyl)amine, *bis*-(triethoxysilylpropyl)ethylene diamine, N-[2-(vinylbenzylamino)ethyl]-3-aminopropyltrimethoxy, and aminoethyl-aminopropyltrimethoxy silane.

9.     The method of claim 1, wherein said silane composition further comprises at least one additional substantially unhydrolyzed silane.

10.    The method of claim 3, wherein said silane composition further comprises at least one substantially unhydrolyzed bis-silyl polysulfur silane.

11. The method of claim 10, wherein said bis-silyl polysulfur silane comprises:



5 wherein each R<sup>1</sup> is an alkyl or an acetyl group, and Z is —Q—S<sub>x</sub>—Q—, wherein each Q is an aliphatic or aromatic group, and x is an integer of from 2 to 10.

12. The method of claim 11, wherein each R<sup>1</sup> is individually chosen from the group consisting of: ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.

13. The method of claim 11, wherein each Q is individually chosen from the group consisting of: C<sub>1</sub> - C<sub>6</sub> alkyl (linear or branched), C<sub>1</sub> - C<sub>6</sub> alkenyl (linear or branched), C<sub>1</sub> - C<sub>6</sub> alkyl substituted with one or more amino groups, C<sub>1</sub> - C<sub>6</sub> alkenyl substituted with one or more amino groups, benzyl, and benzyl substituted with C<sub>1</sub> - C<sub>6</sub> alkyl.

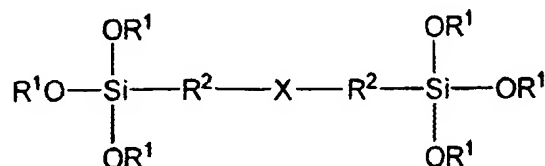
14. The method of claim 10, wherein said at least one bis-silyl polysulfur silane comprises a bis-(triethoxysilylpropyl) sulfide having 2 to 10 sulfur atoms.

15. The method of claim 10, wherein said at least one bis-silyl polysulfur silane comprises bis-(triethoxysilylpropyl) tetrasulfide.

16. The method of claim 10, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane composition is between about 1:10 and about 10:1.

17. The method of claim 10, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane composition is between about 1:3 and about 1:1.
18. The method of claim 10, wherein said silane composition further comprises a non-aqueous solvent.
19. The method of claim 18, wherein said solvent is chosen from the group consisting of: ethanol, methanol, propanol and isopropanol.
20. The method of claim 1, wherein said silane composition consists essentially of at least one substantially unhydrolyzed bis-silyl aminosilane and at least one substantially unhydrolyzed bis-silyl polysulfur silane.
21. The method of claim 20, wherein said silane composition consists essentially of said at least one substantially unhydrolyzed bis-silyl aminosilane, said at least one substantially unhydrolyzed bis-silyl polysulfur silane, and a non-aqueous solvent.
22. The method of claim 10, further comprising the step of drying said coating.
23. The method of claim 1, further comprising the step of adhering a polymer layer to said coating.
24. The method of claim 23, wherein said polymer layer comprises rubber.
25. The method of claim 24, wherein said polymer layer comprises a sulfur-cured rubber.

26. The method of claim 10, further comprising the step of adhering a polymer layer to said coating.
27. The method of claim 26, wherein said polymer layer comprises rubber.
28. The method of claim 27, wherein said polymer layer comprises a sulfur-cured rubber.
29. A method of adhering rubber to a metal substrate, comprising:
- (a) applying a coating of a silane composition onto a metal substrate, said silane composition comprising:
    - a bis-silyl aminosilane, or the hydrolysate or partial hydrolysate thereof; and
    - a bis-silyl polysulfur silane, or the hydrolysate or partial hydrolysate thereof; and
  - (b) adhering rubber to said coating.
30. The method of claim 29, wherein said bis-silyl aminosilane comprises an aminosilane having two trisubstituted silyl groups, wherein the substituents are individually chosen from the group consisting of alkoxy, aryloxy and acyloxy.
31. The method of claim 30, wherein said bis-silyl aminosilane comprises:

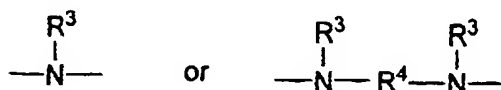


wherein:

-each  $\text{R}^1$  is individually chosen from the group consisting of:  $\text{C}_1$  -  $\text{C}_{24}$  alkyl and  $\text{C}_2$  -  $\text{C}_{24}$  acyl;

-each  $R^2$  is individually chosen from the group consisting of: substituted aliphatic groups, unsubstituted aliphatic groups, substituted aromatic groups, and unsubstituted aromatic groups; and

-X is either:



-wherein each  $R^3$  is individually chosen from the group consisting of: hydrogen, substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and

- $R^4$  is chosen from the group consisting of: substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups.

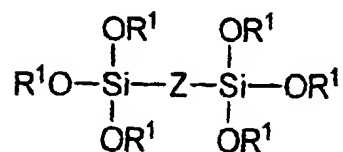
32. The method of claim 31, wherein each  $R^1$  is individually chosen from the group consisting of: ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.

33. The method of claim 31, wherein X is chosen from the group consisting of: a C-Si bond,  $C_1 - C_6$  alkylene,  $C_1 - C_6$  alkenylene,  $C_1 - C_6$  alkylene substituted with at least one amino group,  $C_1 - C_6$  alkenylene substituted with at least one amino group, arylene, and alkylarylene.

34. The method of claim 31, wherein each  $R^2$  is individually chosen from the group consisting of: hydrogen, ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.

35. The method of claim 29, wherein said bis-silyl aminosilane is chosen from the group consisting of: bis-(trimethoxysilylpropyl)amine, bis-(triethoxysilylpropyl)amine, and bis-(triethoxysilylpropyl)ethylene diamine.

36. The method of claim 29, wherein said bis-silyl polysulfur silane comprises:



wherein each  $\text{R}^1$  is an alkyl or an acetyl group, and Z is  $-\text{Q}-\text{S}_x-\text{Q}-$ , wherein each Q is an aliphatic or aromatic group, and x is an integer of from 2 to 10.

37. The method of claim 36, wherein each  $\text{R}^1$  is individually chosen from the group consisting of: ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.

38. The method of claim 36, wherein each Q is individually chosen from the group consisting of:  $\text{C}_1 - \text{C}_6$  alkyl (linear or branched),  $\text{C}_1 - \text{C}_6$  alkenyl (linear or branched),  $\text{C}_1 - \text{C}_6$  alkyl substituted with one or more amino groups,  $\text{C}_1 - \text{C}_6$  alkenyl substituted with one or more amino groups, benzyl, and benzyl substituted with  $\text{C}_1 - \text{C}_6$  alkyl.

39. The method of claim 29, wherein said at least one bis-silyl polysulfur silane comprises a bis-(triethoxysilylpropyl) sulfide having 2 to 10 sulfur atoms.

40. The method of claim 39, wherein said at least one bis-silyl polysulfur silane comprises bis-(triethoxysilylpropyl) tetrasulfide.

41. The method of claim 29, wherein said metal substrate is chosen from the group consisting of:

- zinc and zinc alloys;
- metal substrates having a zinc-containing coating;

- steel;
- aluminum and aluminum alloys;
- copper and copper alloys;
- tin and tin alloys; and
- metal substrates having tin-containing coatings

42. The method of claim 29, wherein the silanes in said silane composition are substantially unhydrolyzed.

43. The method of claim 42, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane composition is between about 1:10 and about 10:1.

44. The method of claim 42, wherein said silane composition further comprises a non-aqueous solvent.

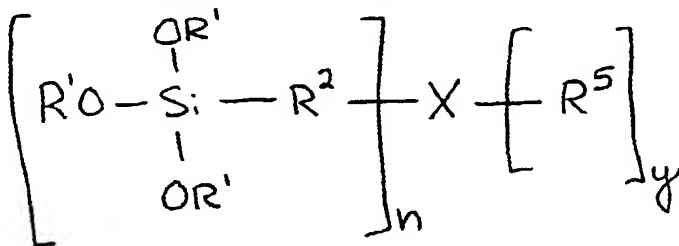
45. The method of claim 29, wherein said silane composition consists essentially of said at least one substantially unhydrolyzed bis-silyl aminosilane and said at least one substantially unhydrolyzed bis-silyl polysulfur silane.

46. The method of claim 29, wherein the silanes in said silane composition are at least partially hydrolyzed.

47. The method of claim 46, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane composition is between about 1:10 and about 10:1.

48. The method of claim 47, wherein said silane composition further comprises water and a solvent.

49. The method of claim 48, wherein the ratio of water to solvent in said silane composition is between about 1:1 and about 1:20.
50. The method of claim 46, wherein the pH of said silane composition is between about 4 and about 7.
51. The method of claim 29, wherein said rubber comprises a sulfur-cured rubber.
52. The method of claim 51, wherein said step of adhering said sulfur-cured rubber comprises applying an uncured rubber compound directly onto said silane coating, and thereafter curing said rubber compound.
53. The method of claim 52, further comprising the step of drying said silane coating prior to applying said uncured rubber compound.
54. A silane composition comprising:  
 -at least one substantially unhydrolyzed aminosilane which has one or more secondary or tertiary amino groups; and  
 -at least one other substantially unhydrolyzed silane
55. The silane composition of claim 54, wherein said aminosilane comprises:



wherein:

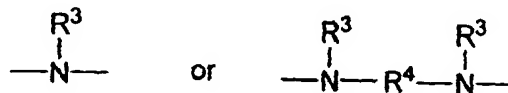
- n is either 1 or 2;  
 -y = (2-n);

-each  $R^1$  is individually chosen from the group consisting of:  $C_1 - C_{24}$  alkyl and  $C_2 - C_{24}$  acyl;

-each  $R^2$  is individually chosen from the group consisting of: substituted aliphatic groups, unsubstituted aliphatic groups, substituted aromatic groups, and unsubstituted aromatic groups;

- $R^5$  is chosen from the group consisting of: hydrogen,  $C_1 - C_{10}$  alkylene,  $C_1 - C_{10}$  alkylene substituted with one or more amino groups,  $C_1 - C_{10}$  alkenylene,  $C_1 - C_{10}$  alkenylene substituted with one or more amino groups, arylene, and alkylarylene;

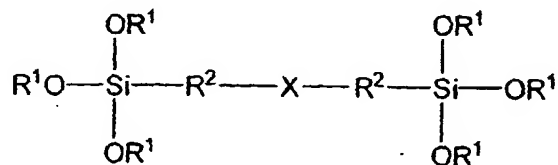
-X is either:



-wherein each  $R^3$  is individually chosen from the group consisting of: hydrogen, substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and

- $R^4$  is chosen from the group consisting of: substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and wherein, when  $n=1$ , at least one of said  $R^3$  and said  $R^5$  is not hydrogen.

56. The silane composition of claim 54, wherein said aminosilane comprises:



wherein:

-each  $R^1$  is individually chosen from the group consisting of:  $C_1 - C_{24}$  alkyl and  $C_2 - C_{24}$  acyl;

-each  $R^2$  is individually chosen from the group consisting of: substituted aliphatic groups, unsubstituted aliphatic groups, substituted aromatic groups, and unsubstituted aromatic groups; and  
 -X is either:



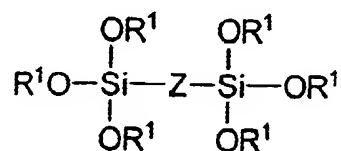
-wherein each  $R^3$  is individually chosen from the group consisting of: hydrogen, substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and  
 - $R^4$  is chosen from the group consisting of: substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups.

57. The silane composition of claim 54, wherein said aminosilane is chosen from the group consisting of: *bis*-(trimethoxysilylpropyl)amine, *bis*-(triethoxysilylpropyl)amine, and *bis*-(triethoxysilylpropyl)ethylene diamine.

58. The silane composition of claim 54, wherein said other substantially unhydrolyzed silane comprises an organofunctional silane.

59. The silane composition of claim 56, wherein said other substantially unhydrolyzed silane comprises a bis-silyl polysulfur silane.

60. The silane composition of claim 59, wherein said bis-silyl polysulfur silane comprises:



wherein each  $R^1$  is an alkyl or an acetyl group, and Z is  $-Q-S_x-Q-$ , wherein each Q is an aliphatic or aromatic group, and x is an integer of from 2 to 10.

61. The silane composition of claim 59, wherein said at least one bis-silyl polysulfur silane comprises a bis-(triethoxysilylpropyl) sulfide having 2 to 10 sulfur atoms.

62. The silane composition of claim 59, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane composition is between about 1:10 and about 10:1.

63. The silane composition of claim 59, wherein said silane composition further comprises a non-aqueous solvent.

64. The silane composition of claim 59, wherein said silane composition consists essentially of said at least one substantially unhydrolyzed bis-silyl aminosilane and said at least one substantially unhydrolyzed bis-silyl polysulfur silane.

65. A silane coated metal substrate made in accordance with the method of claim 1.

66  
73. A metal substrate having a polymer layer thereon, made in accordance with the method of claim 23.

67  
74. A metal substrate having rubber adhered thereto made in accordance with the method of claim 29.

Rule  
126